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Water treatment studies of SPIONs treated with Olive Oil

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ABSTRACT

The significance of nanoparticles for various applications is often assessed by their narrow size distribution, suitable magnetic saturation, better biocompatibility and low toxicity effects. In this work superparamagnetic iron oxide nanoparticles (SPIONs) were synthesized via a co-precipitation technique using ferrous salts with a Fe3+/Fe2+. Olive oil has been used as the coating material, owing to their benefits to the environment. This paper is concerned with the removing chromium from the waste water of electroplating industry by Olive oil mediated iron oxide nanoparticles. The prepared nanoparticles were studied in terms of size, morphology, magnetic behavior, structure, surface area including surface chemical structure and charges using different techniques such as XRD, FTIR and SEM.

Keywords: SPIONs, Olive oil and Water treatment.

1. INTRODUCTION

Magnetic nanoparticles have large surface areas relative to their volume and can easily bind with chemicals and then they be removed using a magnet. This principal way nanotechnologies might help alleviate water problems is by removing water contaminants including bacteria, viruses, pesticides and hazardous heavy metals like arsenic, chromium, Nickel, etc., Heavy metals contaminated waste water from industrial activities such as electroplating, textile dyeing; tanneries etc reach the surface

or ground water sources if it is inadequately treated[1-2]. In addition leaching from solid waste dumps (e.g. fly ash ponds, sludge from above industries) also contributes towards heavy metal accumulation. Polluted water is often treated by conventional or pressure-driven membrane processes to make it comply with drinking water standards. This article analysis the some of low cost, non toxic and sustainable approach for the remediation of waste water released from electroplating industries.

Chromium (Cr) is a transition heavy metal which has two stable forms trivalent Cr (III) and the hexavalent Cr (VI) species. Chromium (III) is an vital nutrient that helps the body use sugar, protein, and fat. (Mertz *et al.*, Walter *et al.*) and it is a very stable oxidation state of chromium. In Chromium (III) state, the chrome is labile and kinetically very slow to react or form complexes. It is not a strong oxidizer and the human's natural body acidity is enough for the chrome to keep to this Cr (III) state. But the hexavalent Cr (VI) species are very harmful it can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum (Cronin *et al*) and the large amount of this hexavalent Chromium is very harmful and it is responsible for many allergic and many other harmful disease (ATDSR report). The harmfulness and hazardous effect is also depend upon the oxidation state of chromium and it has been find that Cr (VI) is more harmful than Cr(III) (Becquer *et al.*, 2003). Therefore here we are using the removal of toxic and heavy metal ions by applying Iron oxide nanoparticles.

Most nanoparticles in various bio applications today are stabilized in nature and therefore studies using virgin nanoparticles may not be relevant for assessing the behaviour of the actually used particles. Stabilization is often used to decrease agglomeration and therefore increase mobility of particles. This stabilization process is further required to be a non-toxic and phosphine free, hence naturally synthesized Oliver oil have been tried here for such stabilization. The Olive oil has the additional benefit that unlikely to cause allergic reactions, and as such can be used in preparations for lipophilic drug ingredients. Further these oil are very rich in oleic acid which is very effective in controlling of heart disease, stroke, cholesterol level and the usage of iron oxide nanoparticles with its coating during the treatment may have the advantage to the blood cells. Olive oil is predominantly a triacylglyceride of long chain fatty acids with free fatty acids (FFA), Polyphenols (Antioxidants), Peroxides, Polycyclic Aromatic Hydrocarbons (PAHs),vitamin K and vitamin E[4-6].

Table 1. Fatty acids content in Olive oil

FattyAcids (%)	Olive oil
Oleic acid	63-81
Linoleic acid	5-15
Palmitic acid	7-14
Stearic acid	3-5

This paper suggests that usage of such carrier oils stabilized superparamagnetic iron oxide nanoparticles in the removal of chromium ions from the waste water [7-13] is not only to remove these harmful ions and also make the treated water is more safe than the chemicals used for coating the nanoparticles for the stabilization such as

polyethyleneglycol (PEG) (Suzuki *et al*., 1995), polyvinyl alcohol(PVA) (Lee *et al*., 1996), polylactic acid(PLA) (Gomez-Lopera *et al*.,2001), polyethylene (Chatterjee *et al*., 2002), block copolymer (Harris *et al*., 2003), dextran (Paul *et al*.,2004), chitosan (Hassan *et al*.,1992) starch (Veiga *et al*., 2000), oleic acid (Chun-Yu Wang *et al*.,2009). But all these stabilizing agents are being derived by chemical treatment and have been used for biomedical applications. Hence there may be chance of harmfulness to the biological system.

2. MATERIAL AND METHODS

2.1 Materials

All the chemicals were of analytical reagent grade and used without further purification. Ferrous sulphate ($FeSO_4$, 99%), ferric chloride ($FeCl_3$, 99%) and Sodium hydroxide (NaOH) were obtained from Merck (India). Olive Oil was received from Falcon (Exporters of Essential Oils), Bangalore, India. Deionized water was used for the reactions at all stages of the synthesis.

2.2 Synthesis of Iron Oxide Nanoparticles

The co-precipitation method was adopted for synthesis of SPIONs. 100 ml of 0.4 mol/L solution $FeCl_3$ and 100 ml of 0.2 mol/L $FeSO_4$ were mixed and dissolved in deionized water. Then 2 mol/L of Sodium hydroxide was added into the above solution and the pH value was maintained between 10-11 with continuous stirring using a magnetic stirrer for 1 hour and a dark precipitation was formed. Similarly four samples were prepared and kept separately. 5 ml of olive oil was taken and heated to 80^0C in hot air oven and added slowly and stirred continuously for 48 hrs. The resulting ferrosoferric hydroxide dehydrates yielded precipitation of the iron oxide particles and they were washed several times with double distilled deionized water and then filtered. Finally it was dried at 150°C for 2 hr and grinded to fine powder.

2.3 Characterization of Iron Oxide Nanoparticles

X-Ray Diffraction (XRD) patterns were recorded with a Philips analytical X-ray diffractometer using CuKα radiation (λ= 1.5406 Å). FTIR spectra were performed and recorded with a Fourier transform infrared spectrophotometer of type Nicolet 870 between 4000 and 400 cm-1 with a resolution of $4cm^{-1}$ The morphologies and compositions of the Fe_3O_4 nanoparticles were examined by Scanning Electron Microscopy (SEM) using a LEO 1455 VP.

3. RESULTS AND DISCUSSION

XRD analyses confirmed that the synthesized nanoparticles were Magnetite (Fe_3O_4) as shown in Figure.1. Six characteristic peaks were marked by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed for both samples reveal that the resultant nanoparticles were Fe_3O_4 with inverse-spinel structure[14]. In the pattern of XRD diffraction, the broad nature of the diffraction bands indicated that SPIONs have small particle sizes. The particle sizes can also be quantitatively evaluated from the XRD data

using the Debye – Scherrer equation and the average particle size of the olive oil stabilized Fe_3O_4 nanoparticles is 22 nm, respectively.

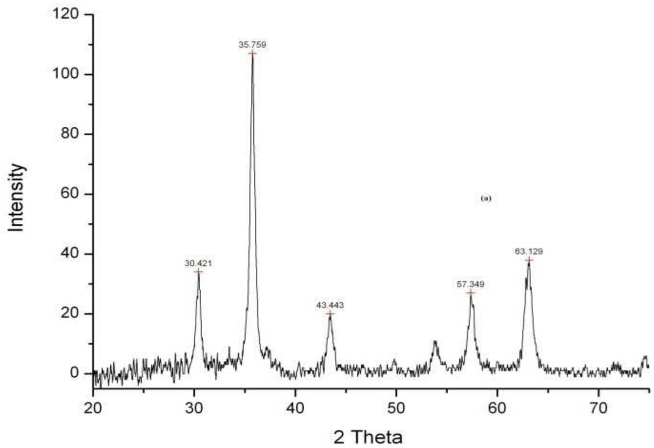


Fig.1. XRD patterns of mediated SPIONs

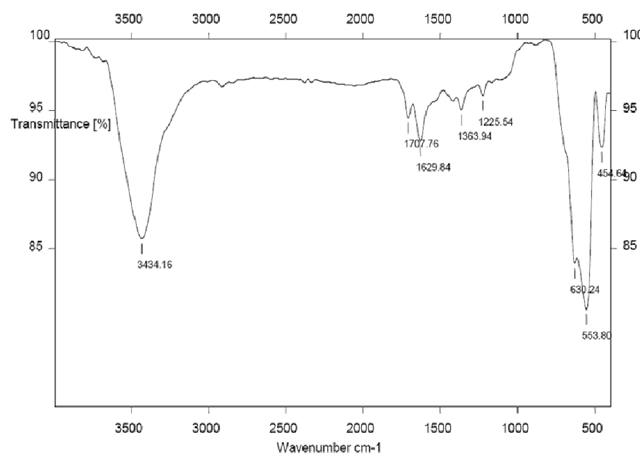


Fig. 2. FTIR of Olive oil Stabilized SPIONs

The successful modification of the nanoparticles surface for their stabilization were confirmed by Fourier Transform Infrared Spectroscopy measurements (FTIR)[15]. The presence of absorption peaks in the region of wave numbers 550-630 cm^{-1} corresponding to the Fe-O vibration. The peaks at 3434 cm^{-1} in fig 2(a) and 3442cm^{-1} in fig 2 (b) were related to the vibrations of -OH and the peaks at 1707 cm^{-1}, 1629 cm^{-1}, 1706 cm^{-1} and 1631 cm^{-1} were due to the overlapping of the absorption bands of the carboxyl groups and double bond of Oleic acid and α–Linolenic acid respectively. The other peaks observed in the region of 882 cm^{-1} - 1366 cm^{-1} were

due to additional compounds (Polyphenols, Peroxides, Polycyclic Aromatic Hydrocarbons (PAHs), vitamin K and vitamin E) present in the oils.

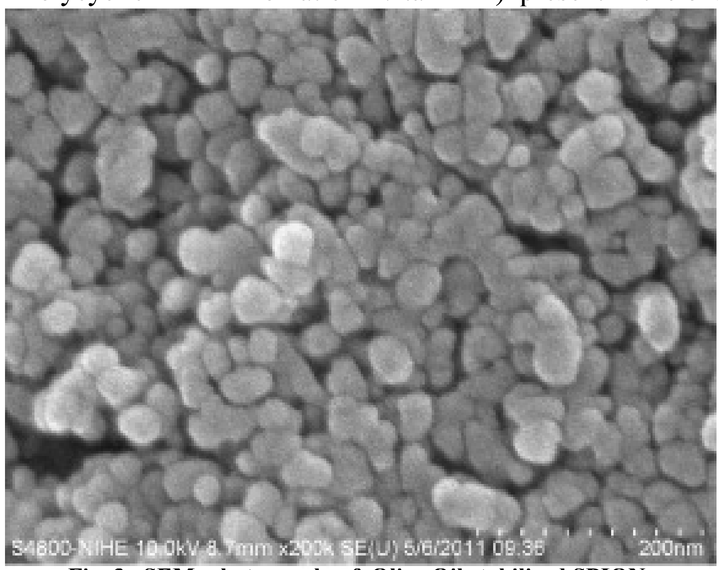
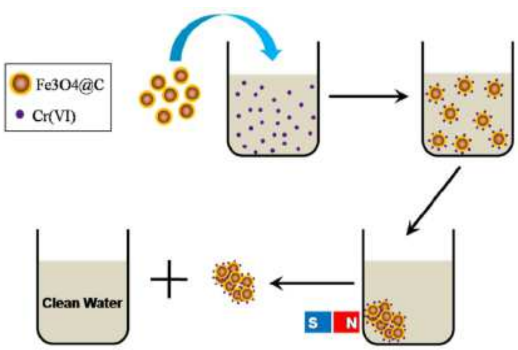


Fig. 3. SEM photograph of Olive Oil stabilized SPIONs

Scanning electron microscopy (SEM) was performed and the particle sizes were analyzed for Olive oil coated nanoparticles.

3.1 Reactives And Materials



Chromium solution is prepared from potassium chromate (K_2CrO_4) salt dissolved into distilled water. Each initial metal standard solution concentration was 1000 mg/L. The initial standard solutions were used in order to evaluate the maximum quantity adsorbed at pH 2.5. The estimation analysis was done for every 10 minutes during 1 hour. The sample containing hexavalent chromium were analyzed by diphenylcarbazide method with a molecular absorption spectrometer (Cintra 202 GBC) with spectral domain between 190 and 1000 nm. Total chromium quantity and the others metals were measured with an atomic absorption spectrometer (GBC 932 AB Plus) with spectral domain between 185 and 900 nm.

3.2 Adsorbent Studies of Iron oxide Nanoparticles

The batch adsorption studies were done by adding each 0.1g of olive oils stabilized Fe_3O_4 in chromium metal solutions. The concentrations of 10mg /L

and 20 mg/ L of each metal solution were taken for adsorption test. The olive oil stabilized SPIONS were dispersed separately by a magnetic stirrer at a speed of 500 rpm. The kinetics of adsorption process was conducted for different intervals of time (between 10 to 60 minutes) at the room temperature (30^{o}C). The nanoparticles separation was carried out by a magnet and 5 ml of each solution was taken every 10 minutes for calculating the metal ion concentration in the remaining solutions. The removal efficiency of Chromium at pH 2.5 is shown in table 2.

Table 2. Removal Efficiency of Hexavalent chromium

Time(Min)	Olive Oil Stabilized SPIONs	
	10 mg/L	20 mg/L
10	83.4	85.6
20	86.8	88.4
30	89.9	89.4
40	92.5	90.6
50	94.6	94.3
60	96.8	97.5

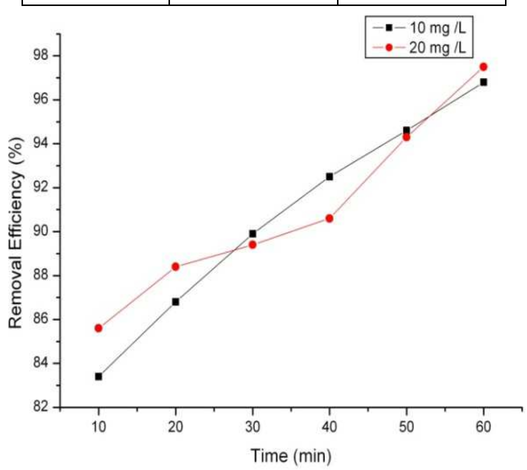


Fig. 4. Removal efficiency of hexavalent chromium adsorbed by Olive oil stabilized SPIONs for 10 mg /L and 20 mg /L concentrations as a function of contact time at pH 2.5

The results shows that efficiency of adsorbents increases slightly for high concentration (20mg/L) of olive oil stabilized iron oxide nanoparticles than the lower concentration. It appears that the removal efficiency of olive oil stabilized Iron oxide nanoparticles is above 90% and adsorption is instantaneous at low pH of 2.5[16].

CONCLUSION

The magnetite nanoparticles with an average diameter of 10 nm were synthesized using a co- precipitation method. These nanoparticles were successfully tested for the removal of some toxic metals from synthetic aqueous solutions, such as hexavalent chromium, copper, cadmium and nickel. The adsorption process was conducted into acidic environment, at pH 2.5. The obtained adsorption data indicated a good adsorption capacity for metal ions removal and a higher adsorption tendency for hexavalent chromium in comparison with the other metal ions. The regeneration of the adsorbents was investigated with good results, in presence of sodium hydroxide solution. The adsorption study showed that the electrostatic attraction was responsible for the metal removal in case of magnetite nanoparticles. The obtained data represents only the preliminary result obtained for achieving a systematic study regarding the removal of heavy metals from wastewaters using as adsorbents the nanoparticles with high capacity of adsorption due theirs high surface area.

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